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Photocatalytic Role of Zinc Oxide Nanoparticles on Synthetic Activated Carbon to Remove Antibiotic from Aquatic Environment

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Background & Aims of the Study: The presence of antibiotics in the environment, especially in aquatic environments is a major concern for health and the environment. The advanced oxidation process due to the ease of use, economical advantages and high performance have attracted a lot of attention. The purpose of this study was Evaluating of the photocatalytic role of zinc oxide on synthetic activated carbon to remove antibiotic from aquatic environment.

Materials & Methods: This experimental study was done in batch reactor that has a 1 L volume. In this study effect of parameters such as initial pH (3-9), initial concentration of cefazolin (20-200 mg/L), modified photocatalyst concentration (20-100 mg/L) and reaction time (10-60 min) was investigated. In this study a low-pressure mercury lamp with the power of 55 watts in stainless case has been used. The cefazolin concentrations in different steps were measured using UV-Vis spectrophotometer in Wavelength of 262 nm.

Results: The results showed that the highest removal efficiency (96%) of cefazolin was at the pH=3, 0.1 mg/L of modified photocatalyst, retention time of 60 min and cefazolin concentrations of 100 mg/L. In the case of changing any of the above mentioned values, process efficiency was decreased.

Conclusion: The results showed that the photocatalytic process of zinc oxide nanoparticles on synthetic activated carbon can be used as an advanced oxidation process to effectively remove pollutants like cefazolin and other similar pollutants.

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Background

Presence of pharmaceutical compounds, in original or metabolized forms in aqueous Environments created increasing concerns a bacterial resistance. The concentration of these compounds could be in range from ng to 10 mg/L (1). The highest antibiotic concentration is associated to pharmaceutical industries wastewater which is in 20-800 mg/L (2). Presence of antibiotics in the environment could affect non-target pathogens, modifying the structure, richness of alga existed in water sources, interferences with plant photosynthesis and creating abnormalities in plant morphology (3-5).

Once antibiotics are released into urban rivers, they often act as parent and still-active compounds in both water and sediment phases (2). They may curb the decomposition capability of sediment, harm aquatic organisms, and promote the development of bacterial resistant genes. Generally, the ecotoxicological effect of antibiotics is closely related to the environmental occurrence, fate and transport in urban rivers. To clarify the sediment–water distribution behavior in rivers is a way to recognize the ecological risk and has drawn increasing attention in recent years (6). Common processes for wastewater treatment are not able to remove these pollutants (7). Among antibiotics, cephalosporin family has high application. Studies show that 50-70 percent of applied antibiotics in Iran are associated to this family (8). Cefazolin is a semi-synthesized antibiotic which applies for treating bacterial diseases like pulmonary infections, bone, stomach, heart and urethra (9). Advanced oxidation processes (AOPs) are based on production of strong oxidizing radicals like hydroxyl radical, sulphate radical, superoxide radical and hydro-peroxyl radical which have great affinity to destruction of antibiotics (10). Over the past years, combined processes such as the use of ozone and hydrogen peroxide, ozone and ultraviolet radiation, the process of ozonation combined with the Fenton process and the catalytic ozonation process have been used (10-12). The optical catalyst oxidation is an advanced technique that completely decomposes the organic pollutants. In this method, an optical source (usually ultraviolet light, UV) is used. In heterogeneous catalytic processes, the reaction materials are not in a same phase and are not easily dissolved in the reaction medium. In order to prevent to decreasing the overall efficiency of the reaction, due to the reduction of the active surface, a bed as the catalyst support, in the present study activated carbon produced from mango seeds with high porosity and active surfaces.

Aims of the study:

The objective of this study was to use UV/AC+ZnO oxidation advanced technology to remove cefazolin antibiotic from aqueous solutions.

Materials & Methods

This experimental study was conducted on a laboratory scale in a discontinuous photochemical enclosure (Batch Reactor). The pilot used (Fig. 1) consisted of a one-liter steel cylindrical photochemical reaction chamber containing a low-pressure mercury lamp by radiation power of 55W. The location of the process was the space between the quartz membrane around the lamp and the steel chamber. The studied samples were synthetic effluents made in laboratory with different concentrations of cefazolin. The parameters including primary pH of the medium (3-9), the modified photocatalyzer (UV/AC+ZnO) concentration (20-100 mg/L), the concentration of cefazolin (20-200 mg/L) and the reaction time (60 min) were investigated. The sample size was calculated using one-factor-at-a-time method (OFAT) and 32 samples were prepared. Each experiment was repeated 3 times.

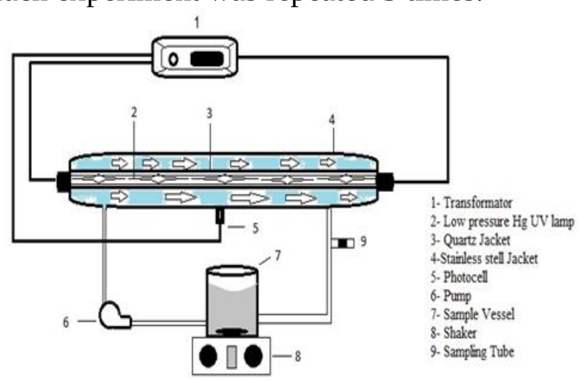

Figure 1) Schematic of studied reactor.

Chemicals:

The chemicals required, such as cefazolin (99.9% purity), sodium hydroxide and sulfuric acid were purchased from Merck and Sigma Aldrich. In the present study, the Senoal pH meter (HACH), centrifuge machine (Sigma) and the DR5000 Spectrophotometer model (HACH) were used. Experiments were performed discontinuously and by changing the pH, irradiation time, initial concentration of cefazolin solution and ZnO-modified with activated carbon concentration. Then, the concentration of residual cefazolin in solutions after the process was measured using a spectrophotometer device at 262 nm (9). After the completion of the experiments, using the obtained results, the optimal values of each parameter were selected and the efficiency of each process was compared by Excel software. Specific tests, including SEM, were performed on activated carbon produced by ZnO nanoparticles to determine the physico-chemical characteristics.

Preparation of activated carbon by chemical-thermal method from seeds of mango fruit:

50 gr of dried mango seeds were mixed with a specific volume of phosphoric acid at a concentration of 95% and a mass ratio of 1:10. The resulting mixture was transferred to a steel reactor of 50 mm in diameter and 250 mm in length and transferred to an electric furnace in a temperature that gradually reached 900 °C for 3 hours. After reaching the temperature of 900 °C, the reactor was kept at this temperature for 1 hour and after 1 hour; the furnace was turned off to slowly reach the ambient temperature. The carbon produced during the above steps was washed with distilled water until the pH value became higher than 6.5. The carbon was placed again at 120 °C for re-drying, and after drying it was crushed using laboratory masonry, passed through 20, 30, 40, and 50 mesh sieves. The remaining sieved carbons were mixed with each other on sieve 30, 40 and 50, and in order to prevent the absorption of moisture in the glass bottle, it was kept in the pack (13).

Modification of produced active carbon via ZnO nano-particles:

Preparation of activated carbon was done by a bonding or hybrid mechanical method, in which specified amounts of active carbon and ZnO nanoparticles (mass ratio of nanoparticles of zinc oxide to activated carbon in the range of 0.1, 0.2, 0.3 and 0.4 mmol/g) was weighed via a digital scale and mixed, then the twice distilled water was added and the magnet was used for full mixing, the process was continued for 24 hours, then after the filtering the mixture, the residual was left to rest on the filter for 24 hours at 95 °C in the oven to dry completely. Finally, all of the above steps resulted in the modified activated carbon (14).

Results

The results of SEM experiments on activated carbon in a modified and unmodified state with a nanoparticle of zinc oxide are presented in Fig. 2.

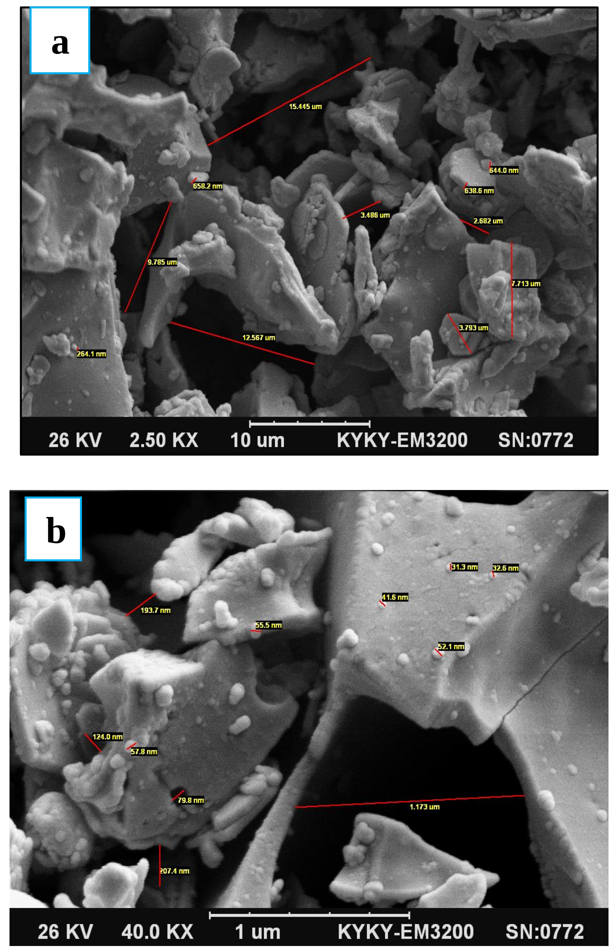

Figure 2) SEM micrographs of activated carbon, a) unmodified, b) modified by ZnO nanoparticles

Effect of pH and contact time:

The effect of pH on the removal efficiency is shown in Fig. 3. In order to evaluate the effect of pH on the process, pH values in the range of 3-9 was evaluated under constant conditions, namely concentration of activated carbon modified by zinc oxide (ratio 0.4 mM of zinc oxide for per gr of active carbon) at a dose of 100 mg/L, the initial concentration of cefazolin at 100 ppm. The results showed that the highest process efficiency has obtained at pH: 3 at the contact time of 60 min and the lowest process efficiency was at pH: 9 at the contact time of 5 minutes.

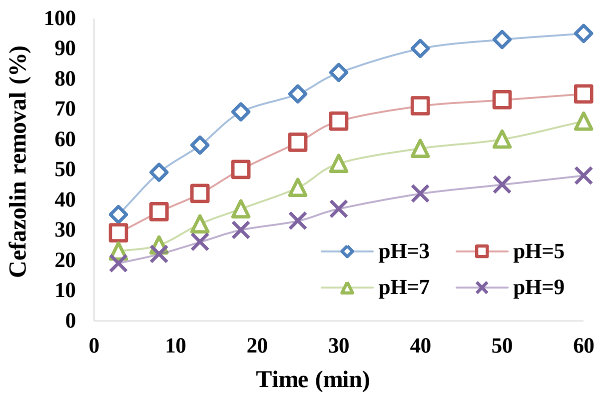

Figure 3) The effect of pH changes on the efficiency of the UV/AC+ZnO process in the removal of cefazolin (modified activated carbon concentration of 100 mg/L, initial concentration of cefazolin 100 mg/L)

The effect of concentrtion of modified active carbon:

The dependence of cefazolin removal on the concentration of modified Photocatalysis at concentrations of 20, 40, 60, 80 and 100 mg/L was investigated, the results of which are shown in Fig. 4. As in the previous step, a parameter was considered as a variable and other parameters (time, pH and optimal cefazolin concentration) were constant. The results of this step showed that the highest efficiency of the process was at the highest concentration of modified activated carbon, so that in the concentration of 100 mg/L of modified activated carbon, 95% efficiency was observed.

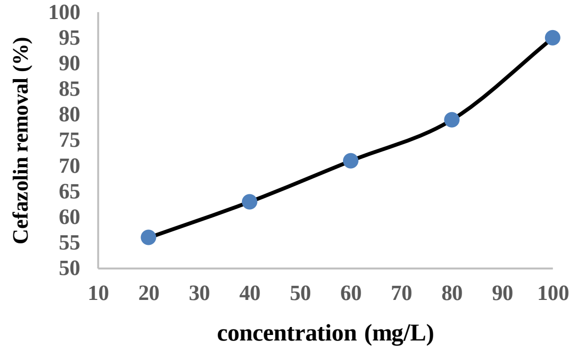

Figure 4) The effect of modified activated carbon changes on the efficiency of UV/AC+ZnO process in removing cefazolin (pH: 3, initial concentration of cefazolin 100 mg/L, 60 minutes)

The effect of changes in the initial concentration of ZnO supported with activated carbon:

Regarding to the dependence of the process efficiency on two parameters of active carbon and zinc oxide nanoparticles together, these two parameters were considered and the results are shown in Fig. 5.

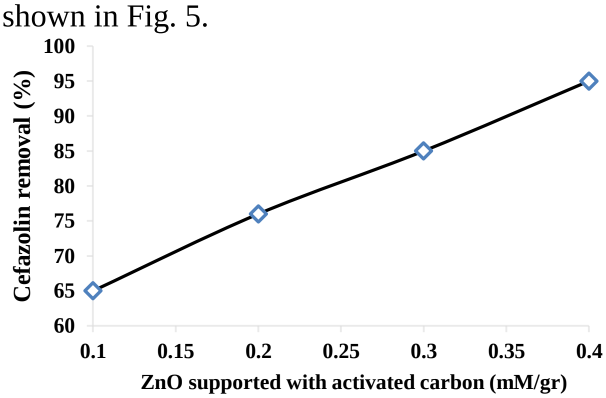

Figure 5) Effect of zinc oxide changes supported with activated carbon to remove cefazolin (pH=3, initial concentration of cefazolin 100 mg/L, 60 min)

Effect of initial concentraion of cefazolin

The effect of changes in the concentration of cefazolin has been studied and the results are shown in Fig. 6. The results showed that the efficiency of the combined process has been reduced by increasing the initial concentration of cefazolin, with the highest efficacy at 20 mg/L and the lowest efficacy in the 200 mg/L concentration.

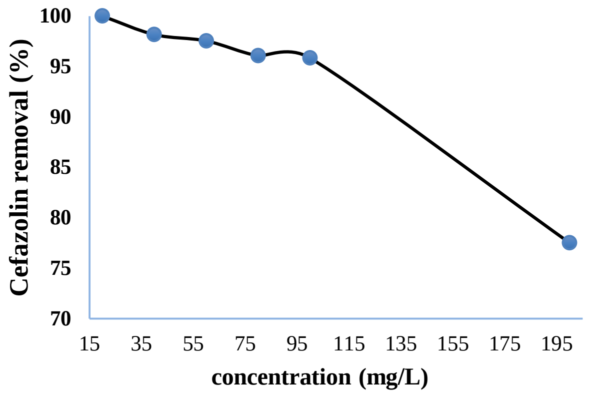

Figure 6) The effect of changes in the initial concentration of cefazolin on the efficiency of the removal of cefazolin (pH=3, modified activated carbon concentration of 100 g/l, 60 minutes)

Discussion

The results of the SEM test showed that the porosity was increased at the surface of synthetic activated carbon, and zinc oxide particles were loaded onto the surface and inside the porous and synthetic activated carbon.

Effect of pH and contact time:

In advanced oxidation, photochemical and processes that are a combination of several processes, pH can be one of the most influential parameters in conducting and determining the efficiency of the process. The results of this study showed that the removal of cefazolin has increased by decreasing the pH so that the desired removal efficiency obtained at pH=3 which is consistent with the study of Shokri et al. (2015). In the study of Shokri et al., The highest rate of cefazolin removal was found in acidic pH (pH=5) (11). Also, in another study by Gurkan et al. (2012) as "Photocatalytic separation of cephazolin by N-Doped TiO_2", the results showed that the max removal of cefazolin observed in acidic pH (9). The reason for increasing the removal efficiency in acidic pH is that, in acidic conditions, the surface of nanoparticles of zinc oxide is positively charged and causes more absorption of cefazolin, resulting in higher absorption of cefazolin by hydroxyl radical production as well as the rate of decomposition in more acidic environments and as a result, elimination efficiency increases.

Reducing the efficiency in the alkaline environment is because that the surface of the nanoparticle has a negative charge and it reduces the absorption of cefazolin, which can reduce the production of hydroxyl radical and reduce the rate of decomposition in the alkaline environment, resulting in reduced efficiency (15). Another reason for the reduction of the process efficiency under alkaline conditions (pH>3) is the chemical properties of cefazolin. Cefazolin is a strong acid, which has a pKa of 3.03, whose chemical structure consists of electrons rich in aromatic rings, and perfectly optimizes the absorption of photocatalytic zinc oxidation with a positive charge and increases the process efficiency.

Effect of concentration of modified activated carbon:

The results showed that by increasing the concentration of modified activated carbon, the rate of cefazolin antibiotic removal increased, with the highest removal rate obtained at 100 mg/L concentration. The reason for increasing the efficiency by increasing the initial concentration of the modified activated carbon can be attributed to the increase of active positions in the active carbon surface, because increasing the initial concentration and increasing the number of active sites causes more absorption of cefazolin pollutant and thus increase the efficiency. Figure 7 schematically illustrates the process involved in this step (16).

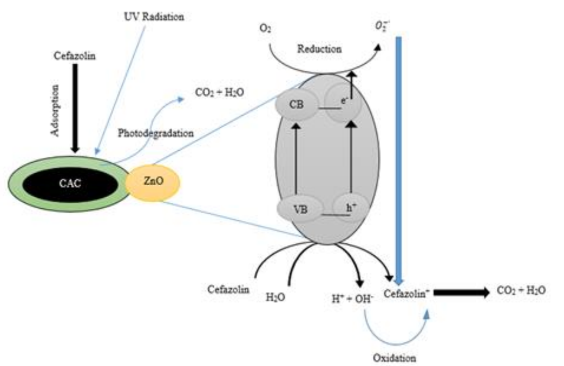

Figure 7) Mechanism of cefazolin antibiotic decomposition in the presence and absence of activated carbon (17).

Effect of changes in zinc oxide concentration on activated carbon:

The results showed that system efficiency was increased by increasing the concentration of nanoparticles of zinc oxide on activated carbon level, which could be due to the increase in active positions created by zinc oxide. Which is in accordance with the results of Samarghandi et al. (18). In these processes, nanoparticles as a catalyst absorb high-energy photons of the ultraviolet spectrum, and subsequently active chemicals, such as hydroxyl radicals, are formed (16). When photocatalyst is exposed to ultraviolet radiation, it stimulates and activates the electron bonding band, and the electrons move from the valence band to the conduction band. The active electron, which is directed to the band, also reacts with organic matter by formation of various radicals such as superoxide or hydroxyl (19).

The effect of changes in the initial concentration of ZnO supported with activated carbon:

The results showed that zinc oxide alone had a lower efficiency compared to that of coated by activated carbon. What is clear at this stage is the role of activated carbon as an important and contributing factor in the process to increase the efficacy of cefazolin antibiotic elimination. Activated carbon, as a secondary factor in addition to zinc oxide, causes more pollutant absorption in the process.

Effect of the initial concentration of cefazolin:

The efficacy of cefazolin removal was reduced by increasing the initial concentration of this pollutant. The reason is that by increasing the initial concentration, more cefazolin molecules are absorbed on the surface of the photocatalyst and the reaction of cefazolin molecules with photonic cavities and hydroxyl radicals prevent from direct contact between them (17). In addition, the high concentration of cefazolin in the environment results in more oxidation of the substance and an increase in the time required for complete purification. The study, conducted by P. Muthirulan et al. (2012), entitled "Photocatalytic role of pure carbon coated with zinc oxide in removing the color of alizarocyanine-cyanine green from aqueous solutions," confirms these results (17).

Conclusion

This process has shown high efficiency in cefazolin removal and the ability of this process to reduce the burden on hospital sewage and pollution-producing industries before entering the treatment units, so final discharged effluent could be treated by conventional treatment processes. This process, due to the lack of sludge and waste production, no persistent organic pollutants production and significant treatment efficiency is environmental friendly.

Footnotes

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Conflict of Interest:

The authors declared no conflict of interest.

References

1. Neisi A, Mohammadi MJ, Takdastan A, Babaeie AA, Yari AR, Farhadi M. Assessment of tetracycline antibiotic removal from hospital wastewater by extended aeration activated sludge. Desalination Water Treat. 2017;80:380-386.
2. Shokoohi R, Leili M, Dargahi A, Vaziri Y, Khamutian R. Common Antibiotics in Wastewater of Sina and Besat Hospitals, Hamadan, Iran. Arch Hyg Sci 2017;6(2):152-159.
3. Azizi E, Ghayebzadeh M, Dargahi A, Hemati L, Beikmohammadi M, Sharafi K. Determination of Effective Parameters on Removal of Organic Materials from Pharmaceutical Industry Wastewater by Advanced Oxidation Process (H_2O_2/UV). Arch Hyg Sci 2016;5(2):69-74.
4. Gu C, Karthikeyan KG, Sibley SD, Pedersen JA. Complexation of the antibiotic tetracycline with humic acid. Chemosphere 2007;66(8):1494-501.
5. Wei R, Ge F, Huang S, Chen M, Wang R. Occurrence of veterinary antibiotics in animal wastewater and surface water around farms in Jiangsu Province, China. Chemosphere 2011;82(10):1408-14.
6. Guo X, Feng C, Zhang J, Tian C, Liu J. Role of dams in the phase transfer of antibiotics in an urban river receiving wastewater treatment plant effluent. Sci Total Environ 607–608 (2017) 1173–9.
7. Andreozzi R, Campanella L, Fraysse B, Garric J, Gonnella A, Lo Giudice R, et al. Effects of advanced oxidation processes (AOPs) on the toxicity of a mixture of pharmaceuticals. Water Sci Techno 2004;50(5):23-8.
8. Kümmerer K. Antibiotics in the aquatic environment – A review – Part I. Chemosphere 2009;75(4):417-34.
9. Gurkan YY, Turkten N, Hatipoglu A, Cinar Z. Photocatalytic degradation of cefazolin over N-doped TiO2 under UV and sunlight irradiation: Prediction of the reaction paths via conceptual DFT. Chem Eng J 2012;184:113-24.
10. Almasi A, Dargahi A, Mohamadi M, Biglari H, Amirian F, Raei M. Removal of Penicillin G by combination of sonolysis and Photocatalytic (sonophotocatalytic) process from aqueous solution: process optimization using RSM (Response Surface Methodology). Electronic physician 2016;8(9):2878.
11. Shokri M, Isapour G, Behnajady MA, Dorosti S. A comparative study of photocatalytic degradation of the antibiotic cefazolin by suspended and immobilized TiO2nanoparticles. Desalination Water Treat 2015;57(27):12874-81.
12. Zhang J, Meng J, Li Y, Hu C. Investigation of the Toxic Functional Group of Cephalosporins by Zebrafish Embryo Toxicity Test. Arch Pharm (Weinheim) 2010;343(10):553-60.
13. Ahmad AA, Hameed BH. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. J Hazard Mater 2010;175(1-3):298-303.
14. Fen L, Bo Y, Wei J, Zhenlong G. Preparation of Activated Carbon Loading Nano-ZnO and Desulfurization Properties under Room Temperature. In: Zhang W, editor. Software Engineering and Knowledge Engineering: Theory and Practice: Selected papers from 2012 International Conference on Software Engineering, Knowledge Engineering and Information Engineering (SEKEIE 2012). Berlin, Heidelberg: Springer Berlin Heidelberg; 2012. p. 177-83.
15. Kumar H, Rani R. Structural and Optical Characterization of ZnO Nanoparticles Synthesized by Microemulsion Route. Int Letters Chem Phys Astron 2013;14:26-36.
16. Muruganandham M, Swaminathan M. Decolourisation of Reactive Orange 4 by Fenton and photo-Fenton oxidation technology. Dyes Pigm 2004;63(3):315-21.
17. Muthirulan P, Meenakshisundararam M, Kannan N. Beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of alizarin cyanin green dye in aqueous solution. J Adv Res 2013;4(6):479-84.
18. Samarghandi MR, Siboni M, Maleki A, Jafari SJ, Nazemi F. Kinetic Determination and Efficiency of Titanium Dioxide Photocatalytic Process in Removal of Reactive Black 5 (RB5) Dye and Cyanide from Aquatic Solution. J Mazandaran Univ Med Sci 2011;21(81):44-52.
19. Daneshvar N, Aber S, Seyed Dorraji MS, Khataee AR, Rasoulifard MH. Photocatalytic degradation of the insecticide diazinon in the presence of prepared nanocrystalline ZnO powders under irradiation of UV-C light. Sep Purif Technol 2007;58(1):91-8.